Kinetic Study on Pyrolysis and Combustion of Palm Emply Fruit Bunches (EFB) by Using TGA Analysis

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KINETIC STUDY ON PYROLYSIS AND COMBUSTION OF PALM EMPTY FRUIT BUNCHES (EFB) BY USING TGA ANALYSIS

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ABSTRACT

Pyrolysis and combustion of palm empty fruit bunches (EFB) were studied by using thermogravimetric analyzer (TGA). The non-isothermal pyrolysis of EFB was performed from ambient temperature up to 900 °C at heating rates of 5, 15, 30 and 40°C/min in N_2 atmosphere. The apparent activation energy of pyrolysis varied linearly with heating rate. The kinetics of EFB combustion is investigated by means of isothermal TGA and measurements were carried out for different fixed temperatures between 500°C and 700°C in O_2 atmosphere. The isothermal and non-isothermal conditions allow the kinetic constants (activation energy, pre-exponential factors and order of reaction) to be estimated by means of the analytical solution of the mass conservation equations. Thermal degradation rates in the first reaction zone were significantly higher than those in the second reaction zone. The apparent activation energies were in the range of 117.25-120.16 kJ/mol and 17.767 kJ/molfor the pyrolysis and combustion respectively. The frequency factor, A for pyrolysis ranged from $4.24 \times 10^{8} s^{-1}$ to $1.33 \times 10^{9} s^{-1}$. And for combustion, frequency factor was $1.08 \times 10^{-1} s^{-1}$

Keywords: Pyrolysis, Combustion, Activation Energy, Frequency Factor, TGA Analysis

1. INTRODUCTION

Empty Fruit Bunches (EFB), as one source of biomass, has traditionally been an important source of energy particularly attractive nowadays because of its inherent nature of being environmentally friendly and renewable. There are compelling reasons for supporting the use of EFB as a source of fuel for Renewable Energy (RE) power generation. Although the current uses of EFB as mulch do have financial benefits, there are better financial gains, with a number of other advantages when used as a fuel for RE power generation. The rapid depletion of fossil fuel needs an alternate replacement and most developed nations are pursuing the development of biomass, an alternate method of power generation.

EFB is the residual bunch after removal of the fruits; it constitutes 20% to 22% of the weight of the fresh fruit bunches. It is consisted of vascular bundles which are embedded in parenchyma tissues are similar to that found in the trunks and fronds. The vascular bundles of empty fruit bunches are quite springy and flexible. On average, fresh EFB from the mill contains 30.5% lignocellulose, 2.5% oil and 67% water [10].

At the palm oil mill, the empty bunches are mainly incinerated to produce bunch ash which contains a high percentage of potassium. The ash is distributed back to the field as fertilizer for the palms. However, the incineration process results in severe air pollution problems. In some oil palm mills, the empty bunch are pressed to reduce their moisture content and burnt as fuel to generate steam to be sold to nearby factories.

In Malaysia fortunately, the country has a ready source of biomass in empty fruit bunches. In Malaysia alone, 9.9 Mte of solid wastes consisting of the oil-palm empty fruit bunch (EFB), fiber, and shell are generated every year. It is conveniently collected and available for exploitation in all palm oil mills. All that needs to be done is to convert the energy in the fuel in the most efficient manner and the country is well on the way to pursue this most important and sustainable renewable source of the energy of the future.

The pyrolysis process is very important, since it controls the ignition, temperature and stability of the flame, and these, ultimately, affect the subsequent burnout of the solid carbon. Understanding the kinetics of char oxidation is useful for the understanding, design and modeling of industrial processes. Also, this aspect may serve as an index to compare different coals and coal blends and predict process performance based on the reactivity parameters estimated.

A few reports have been published concerning the use of wood and palm oil solid waste for an industrial application [1-3]. Most studies have investigated the behavior of pyrolysis of cellulosic materials under nitrogen atmosphere. Most recent models of pyrolysis and combustion of biomass are reviewed by Di Blasi and Colomba [10]. Experimental and theoretical studies on kinetics of pyrolysis of wood branches and leaves have also been

conducted [11, 12]. Experiments on pyrolysis of pine and oak under different oxygen concentrations such as 0%, 10.5% and 21% were carried out by M.X. Fang et al. [1]. Additional studies on pyrolysis of cellulose, hemi-cellulose and lignin under nitrogen, air and pure oxygen atmosphere have been compared [14].

2. METHODOLOGY

The oil-palm empty fruit bunch fiber used in this study was supplied by West Palm Mill, Pulau Carey. As-received palm empty bunches were dried to remove free moisture absorbed during land dumping and then kept for further testing. The pre-dried samples were crushed and sieved to several size fractions. Sample of 250μm of particles sizes was used in the TGA runs. Typically, for the sample size less than 2 mm was primarily fine particles which the reaction is purely reaction kinetics controlled [2]. The pyrolysis and combustion of palm shell was carried out using NETZSCH Thermal Analyzer STA 409C.

Prior to experiments, the thermal analyzer was calibrated for temperature readings and buoyancy effects. About 10 mg of sample was placed in a platinum pan and heated in an inert atmosphere of nitrogen gas over a temperature range of 20–400°C at controlled heating rates of 5, 15, 30 and 40°C/min for pyrolysis. Purified nitrogen (99.9995% purity) at a constant flow rate of 20cm^3/min was used as the purge gas to provide an inert atmosphere for pyrolysis and to remove any gaseous and condensable products evolved, thus minimizing any secondary vapor-phase interactions. At temperature 400°C, air is supplied for combustion of EFB and heating it till temperature 900°.

In the combustion test, this methodology is followed to reach the isothermal stage in the pre-heated EFB without any intra-particle gradients and in order to shorten the first thermal dynamic stage. It was conducted in a dry air atmosphere over a temperature range 500–700°C at a heating rate of 40°C min^{-1}. The subsequent thermal decomposition is carried out in isothermal conditions during 50 min. The same experiment is repeated for five fixed temperatures (T = 500, 550, 600, 650, 700°C). In order to assess the reproducibility, experiments were performed twice

The sample weight loss percent (SWLP), sample temperature and heating effect were continuously recorded as a function of heating time. The heating effect was taken into account when recording sample temperature. So the SWLP can be a function of both sample temperature and heating time. From the SWLP, the mass loss fraction of sample can be obtained. From the mass loss percent, the rate constant of reactions can be estimated. And the kinetic parameters such as activation energy and frequency factor can further be determined.

3. RESULTS AND DISCUSSION

3.1. TGA ANALYSIS ON PYROLYSIS

As is known, biomass such as EFB contains three major macromolecular constituents, namely cellulose, hemicellulose, and lignin. FIG. 1 shows that TGA curve of EFB in N_2 atmosphere in which the pyrolysis process takes place between 200^{0}C and 600^{0}C. It can be clearly seen that weight loss starts around 200^{0}C and almost finishes at 600^{0}C. The maximum decomposition rate was in the temperature ranges of 240 – 350^{0}C.

The conversion of EFB is similar to wood powder in which the following steps are included: (a) desorption of adsorbed water up to 150^{0}C [3], (b) splitting off of cellulose and hemicellulose structure water between 150 – 240^{0}C, (c) in the temperature range be 240 – 400^{0}C, major weight loss takes place due to decomposition of hemicellulose, cellulose and lignin., (d) Further weight loss of EFB between 350 - 550^{0}C was attributed to further devolatilization of residual charcoal from the EFB.

3.1.1. Estimation of Kinetic Parameters of Pyrolysis

From the raw data, the pyrolysis data is focused. From these data the mass loss fraction, α was determined as,

$$\alpha = \frac{m_i - m_t}{m_0 - m_\infty} \tag{1}$$

where m_i is the mass in time t, m_i is initial mass and m_∞ is mass at infinite time.

The kinetics of pyrolysis of solid-state reaction could be described by first order Arrhenius law. In this paper, it is assumed that process of pyrolysis and combustion was divided into two steps (low and high temperature) and each was governed by Arrhenius law [1].

$$\frac{d\alpha}{dt} = kf(\alpha) \tag{2}$$

where

$$k(T) = A\exp\left(-\frac{E}{RT}\right) \tag{3}$$

$$f(\alpha) = (1-\alpha) \tag{4}$$

A is frequency or pre-exponential factor of pyrolytic process, E is the activation energy of pyrolytic process, R is the universal gas constant, T is the absolute temperature and n is the order of reaction. Assuming reaction order for pyrolysis is first order, n = 1

Eqn (2) could be transferred to

$$\frac{d\alpha}{f(\alpha)} = \frac{k}{\beta}dT \tag{5}$$

An integration function of Eqn (5) is shown as below

$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_o}^{T}\exp\left(-\frac{E}{RT}\right)dT \tag{6}$$

Eqn (6) is integrated by using Caots-Redfern method [3, 5] and becomes:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{R}\frac{1}{T} \quad (7)$$

where

$$g(\alpha) = -\ln(1-\alpha) \quad (8)$$

The term of $\ln[g(\alpha)/T^2]$ varies linearly with 1/T as slope of the line is -E/R. The intercept of the line with y-axis is related to the pre-exponential factor, A. Both the activation energy E and pre-exponential factor A can be determined by the slope and intercept of the line. However, pyrolysis process was considered to be a single reaction in this analytical method. Thus, activation energy calculated was an average value and a little smaller than methods [1].

Using the data from the pyrolysis thermograms (FIG 2), the kinetic parameters including activation energy, E and the frequency factor A, were estimated with high correlation coefficients (all above 0.98) by using different heating rate listed in TABLE 2. As the heating rate was increased, the activation energy remained relatively constant, but the frequency factor was dependent on heating rate, increasing progressively from 4.24×10^8 to $1.33 \times 10^9 s^{-1}$. The higher heating rate, the easier and faster would be the pyrolytic reaction [2]. The assumed first order reaction was satisfied as the correlation coefficient was more than 0.98. From TABLE 3, the kinetic parameters for EFB are quite close to other same types of lignocellulosic biomass such as woodchips, palm shell and cotton residues.

The Arrhenius parameters derived from TGA data are for a global model, which include multiple reaction steps, diffusion of gases and ions, evaporation, and interface effects. Thus the "apparent" Arrhenius parameters were used to avoid ambiguity [1].

The kinetics of the thermal decomposition can be modeled by a scheme consisting of three independent first-order parallel reactions of the main biopolymer components: hemicellulose, cellulose and lignin. It was suggested the kinetic model of pyrolysis was the simple one-step global model [2]:

$$\text{EFB (biomass)} \xrightarrow{k} \text{Char} + \text{Volatiles} \quad (9)$$

k is function of remaining original raw material and follow an Arrhenius law.

The major volatiles evolved during the lower temperature pyrolysis (were CO, CO_2 and H_2O while CO, CO_2, H_2O, H_2, CH_4 and C_2H_6 were evolved in higher temperature pyrolysis [2].

3.2. TGA ANALYSIS ON COMBUSTION

Refer to FIG 6, TGA run isothermally at temperature of 500^0C was carried out in two phases. The first stage was the non isothermal TGA run, which was under gas N_2 atmosphere from 25 - 500 ^{0}C with a fixed heating rate, 40^0C/min. This is to ensure devolatilization effects will not affect the residual char combustion after undergoing pyrolysis.

The second stage was the isothermal TGA run, which was under air flow rate at a fixed temperature, 475^0C for 35 minutes. The combustion then took

place until the char was finally become ash. From FIG 6, it is obvious that rate of pyrolysis is higher than rate of combustion since the mass of residual char after pyrolysis is little to be used for combustion.

3.2.1. Estimation of Kinetic Parameter of Combustion

Rate of decomposition of empty fruit bunches char can be described as [7]:

$$-\frac{dm}{dt} = km^n \tag{10}$$

where dm/dt is rate of mass change in time t, k is rate constant, m is mass of sample in time

In order to find out the value of n and k of each isothermal run, Eqn (10) becomes:

$$\ln\left(-\frac{dm}{dt}\right) = \ln k + n \ln m \tag{11}$$

Plot of ln[-dm/dt] versus ln(m) will yield a straight line with reaction order equals to the slope and the intercept-Y is ln k.

In order to estimate the frequency factor A and activation energy E, Eqn (2) becomes:

$$\ln k = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \tag{12}$$

Plot of ln k versus 1/T will yield a straight line with the slope equals to – E/R and the Y-intercept equals to ln A.

From Arrhenius plot of FIG 12, slope = -2137 and Y-intercept = 1.8714. Activation Energy, E = 2137 x 8.314 = 17.767 kJ/mol, and Frequency factor, A = exp(1.8714) = 6.497 min^{-1} = 1.08 $x10^{-1}$ s^{-1}.

The reaction order of combustion for all the isothermal sets were smaller than 1which was ranged from 0.72 to 0.39. Average of reaction order for combustion is 0.57. The reaction order decreased from 500^0C to 700^0C isothermal set. The higher isothermal temperature conducted the available residual mass of char for combustion is lesser due to devolatilization occurred. The reaction order was depending on the mass sample available for Eqn 9.

The activation energy of combustion is relatively small (17.77kJ/mol) compare to activation energy of pyrolysis (120.16 kJ/mol). The pyrolysis reaction is an endothermic process which heat is required to break down the structure of rigid cellulose and lignin in order to release volatile gases. Combustion is an exothermic process which heat is released during combustion occurred. The reaction with higher activation energy has the smaller pre-exponential factor. The pre-exponential factor for pyrolysis was 8.03 $x10^8 s^{-1}$ while for isothermal combustion in this case was 1.08 $x10^{-1}$ s^{-1}.

The rate constant of combustion reaction is relatively smaller than pyrolysis reaction since rate of thermal decomposition of residual char is smaller than pyrolysis.

A simple kinetic model was suggested in char combustion.

$$\text{Char} \overset{k}{\Rightarrow} CO_2 + H_2O \tag{13}$$

where k is function of remaining char and obeyed the Arrhenius law.

From TABLE 4, the BPL char (a steam activated carbon) which was derived from bituminous coal has lower reactivity values compare to EFB char. Which means the EFB char is a good combustion material that gives a higher reactivity or rate constant. During the oxidation initiated, it was assumed that all the EFB chars contain no volatiles materials that affected the TGA result. However, there was a handful of volatile gas that released during the combustion. Thus, the results of isothermal TGA were not accurate like in non-isothermal pyrolysis.

4. CONCLUSION

The TG curves of EFB showed two different weight loss regimes due to the decomposition of the bio-polymers and devolatilization of residual charcoal during pyrolysis conducted. For pyrolysis, the range of apparent activation energies determined by the differential method was between 116 – 220 kJ/mol. The frequency factor increased progressively from 4.24 $x10^8$ to 1.33 $x10^9 s^{-1}$ from heating rate 5 to 40 K/min. The order of reaction was assumed to be first order.

For isothermal combustion, simple kinetic approach was used which applying Arrhenius law of reaction. The apparent activation energy of residual char EFB is 17.767kJ/mol. The rate constant, k was increasing with temperature, which implied that the combustion reaction was a pure kinetic controlled process.

The residual carbon of the present EFB is 17wt%. In the literature, it has been reported to vary from about 10 to 40 wt%, which is in the range of a typical biomass [16]. Generally, higher percentage of residual carbon that is found in residue, the more unburned carbon that can be found in the exhaust gas.

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TABLE 2: One-steps kinetic parameters for the pyrolysis of palm empty fruit bunches

Heating rate, β (K/min)	**Activation Energy, E (kJ/mol)**	**Frequency factor, A (s^{-1})**	**Correlation coefficient, R^2**
5	117.60	4.24×10^8	0.9825
15	117.25	6.73×10^8	0.9863
30	116.80	7.85×10^8	0.9932
40	120.16	1.33×10^9	0.9926

TABLE 3: Kinetic parameters of pyrolysis of different types of sample [1, 11]

Sample	***Activation Energy, E (kJ/mol)***	***Frequency factor, A (s^{-1})***
Forest	130.0	1.03×10^7
Cotton	149.9	7.58×10^9
Woodchips	145.3	1.19×10^8
Palm shell	114.3	2.33×10^9
EFB	118.0	8.03×10^8

TABLE 3: Arrhenius plot data of various isothermal run of TGA

T(C)	**T(K)**	**n**	**ln k**	**1/T**	**R^2**
500	773.15	0.715	-0.895	0.001293	0.9796
550	823.15	0.657	-0.794	0.001214	0.9774
600	873.15	0.625	-0.585	0.001145	0.9506
650	923.15	0.489	-0.442	0.001083	0.9669
700	973.15	0.385	-0.330	0.001027	0.9702

TABLE 4: Reactivity values of Coal Char of BPL and EFB

BPL Coal Char [5]		***EFB Coal Char***	
Temperatures	**Reactivity, k**	**Temperatures**	**Reactivity, k (s^-**
475	0.0383	500	6.811
500	0.0642	550	7.534
525	0.1558	600	9.288
550	0.2526	650	10.712
575	0.3422	700	11.987

FIGURE 1: *TGA curve for pyrolysis of EFB for heating rate, 15K/min*

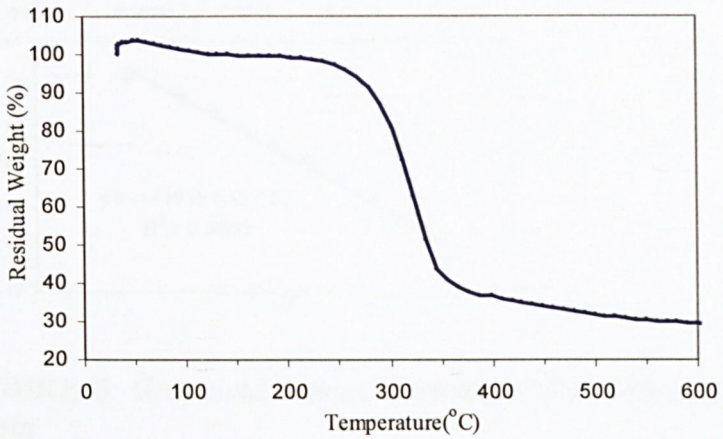


FIGURE 2: *Residual Weight Percent of EFB undergoing pyrolysis at various heating rates*

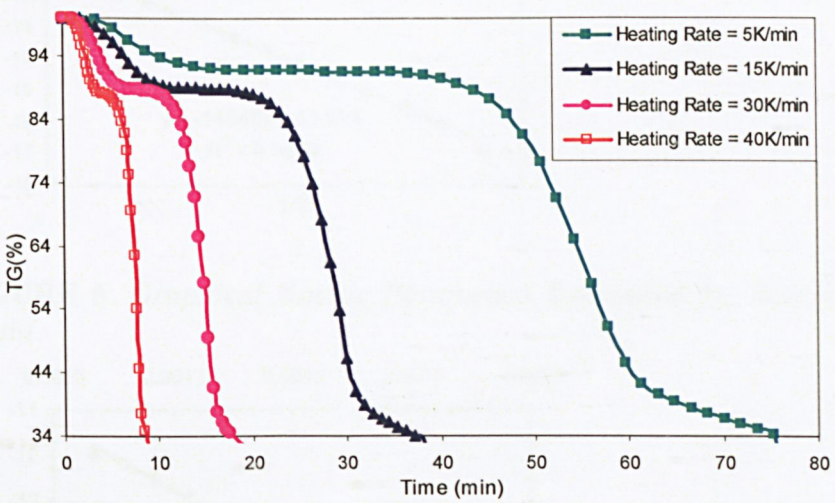


FIGURE 3: *Graphical Kinetic Parameters Estimation for heating rate, 5 K/min*

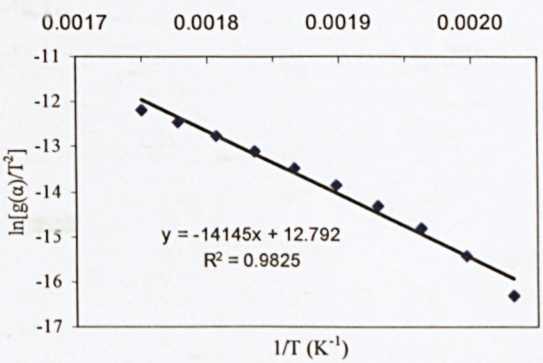


FIGURE 4: *Graphical Kinetic Parameters Estimation for heating rate, 15 K/min*

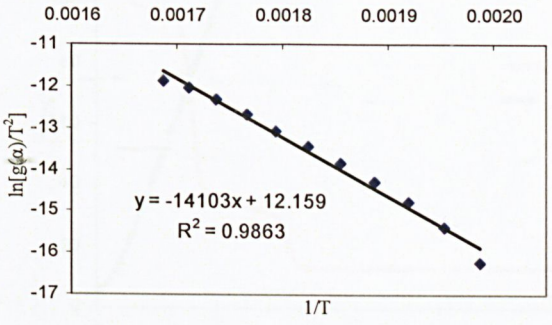


FIGURE 5: *Graphical Kinetic Parameters Estimation for heating rate, 20 K/min*

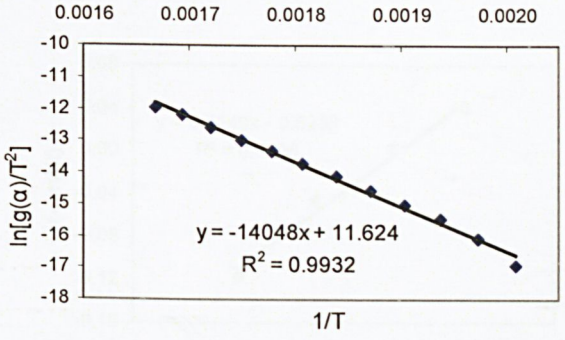
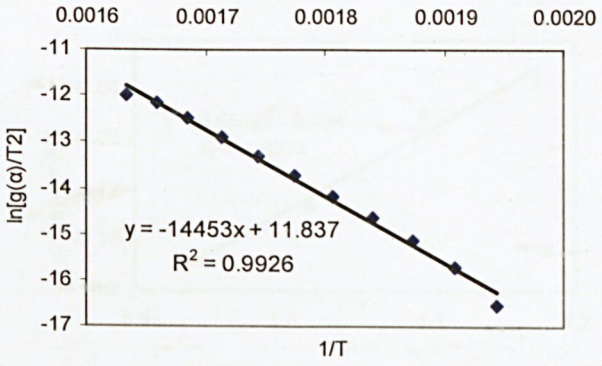


FIGURE 6: *Graphical Kinetic Parameters Estimation for heating rate, 40 K/min*



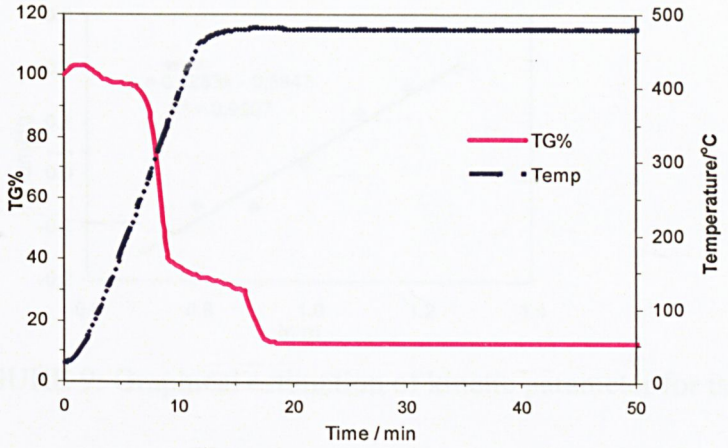


FIGURE 6: TGA curves for pyrolysis and combustion for heating rate, 40 K/min

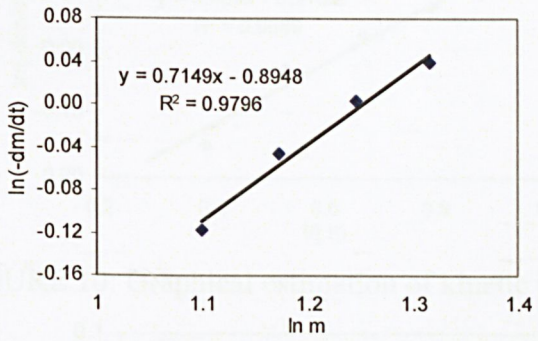


FIGURE 7: Graphical estimation of kinetic parameter for isothermal 500^0C

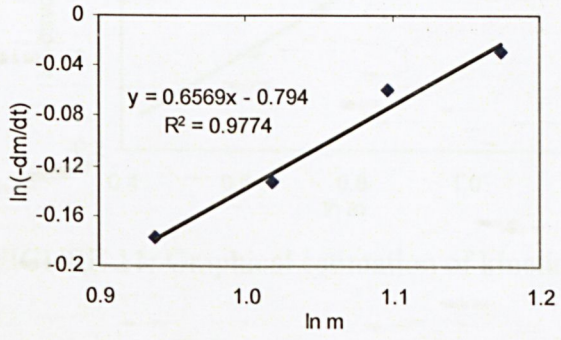


FIGURE 8: Graphical estimation of kinetic parameter for isothermal 550^0C

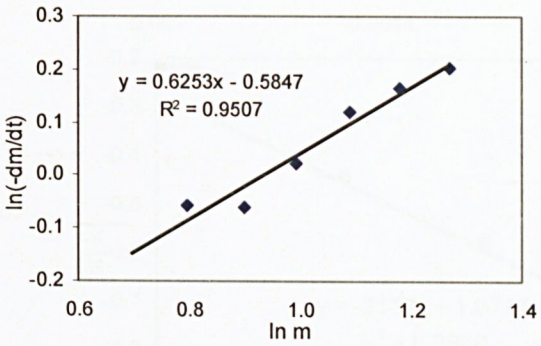


FIGURE 9: Graphical estimation of kinetic parameter for isothermal 600^0C

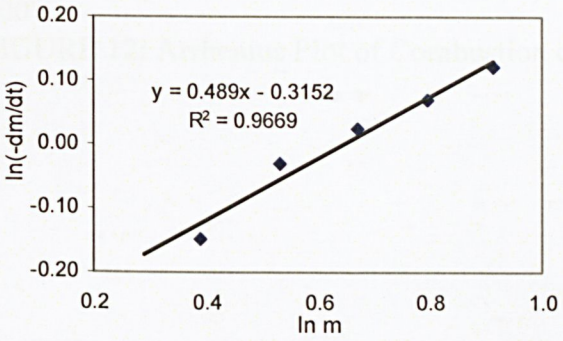


FIGURE 10: Graphical estimation of kinetic parameter for isothermal 650^0C

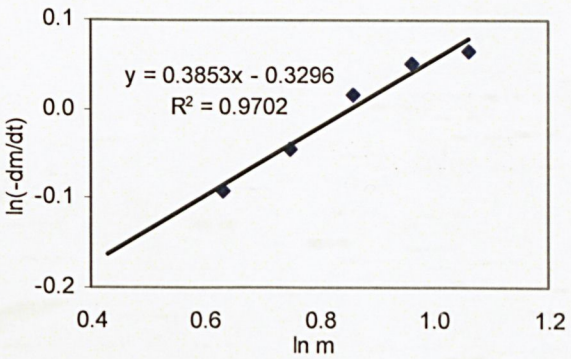
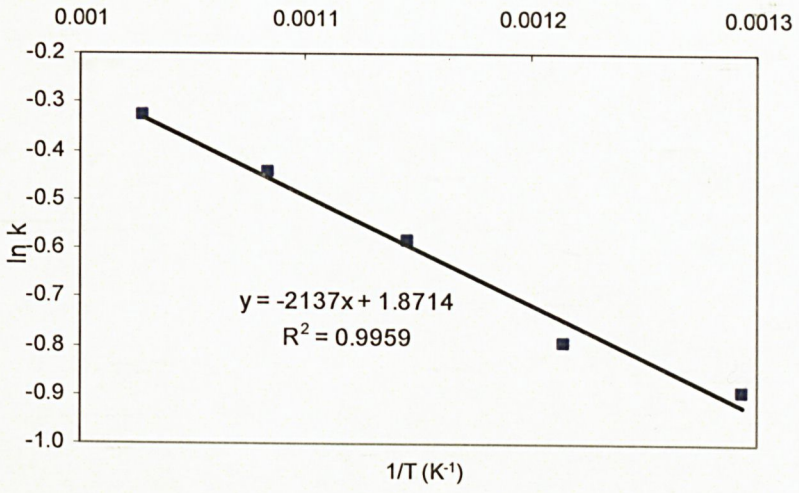


FIGURE 11: Graphical estimation of kinetic parameter for isothermal



700^0C

FIGURE 12: Arrhenius Plot of Combustion of EFB